CEMENT AND LIME

MANUFACTURE

The Structure of Tricalcium Aluminate.

SOME recent work on the structural relations of $Ca_3Al_2O_6$ to other compounds and on the structure of glass in Portland cement is described by Mr. H. F. McMurdie in Research Paper No. 1437 of the United States National Bureau of Standards. The following is an abstract of the paper.

Structural Relations of $Ca_3Al_2O_6$ to other Compounds.

The diffraction data for $Ca_3Al_2O_6$ obtained in this laboratory are given in *Table* 1*. This material was prepared by heating 62·2 per cent. of CaO and 37·8 per cent. of Al_2O_3 just below 1,450 deg. C. for four hours. The material was then ground and reheated. This was repeated until petrographic examination indicated that the sample contained over 95 per cent. of one phase. These diffraction data indicate a cubic unit cell with $a_0 = 15·24$ A, in agreement with the findings of Lagerquist and co-workers. On the basis of this cell all the observed lines were indexed, including several first-order lines which could not result from a unit cell with $a_0 = 7·62$ A.

Examination of these data revealed that the stronger lines considered alone defined a body-centred cubic structure with $a_0 = 3·81$ A. A similarity between these strong lines and those of other compounds has been noted by several workers. In the present investigation it has been found that the compounds of the cristobalite type[1] give a similar series of strong lines. Included in this group of compounds are high cristobalite (SiO_2), alpha carnegieite ($NaAlSiO_4$), and Na_2CaSiO_4. The strong lines of the last compound are most similar to those of $Ca_3Al_2O_6$. $Na_4Ca(SiO_3)_3$ and $Na_2Ca_3(SiO_3)_3$ also have a series of strong lines somewhat similar to those of $Ca_3Al_2O_6$.[2] From a consideration of the similarity of the strong lines of the pattern of $CaTiO_3$, Na_2CaSIO_4, and $Ca_3Al_2O_6$, it may be assumed that they have some structural characteristics in common. Previous

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*In all patterns made for this paper, $CuK\alpha$ radiation was used with cylindrical cameras having a radius of about 5·7 cm.

TABLE 1.

POWDER DIFFRACTION DATA ON $Ca_2Al_2O_6$ (Cubic $a_0 = 15\cdot24 \pm 0\cdot02$ A).

[VS = very strong; VW = very weak; M = medium; S = strong; W = weak]

Estimated intensity	d	hkl	Estimated intensity	d	hkl
W	4.08	123	VW	1.951	650-643
VW	3.34	124	S	1.907	800
VS	2.70	440	VW	1.826	653
W	2.39	620	S	1.556	844
VW	2.258	630-542	M	1.346	880
M	2.200	444	M	1.206	12.40
VW	2.039	642	W	1.106	888
VW	1.984	731-553	M	1.023	12.84

TABLE 2.

POWDER DIFFRACTION DATA ON $CaTiO_3$ (Cubic $a_0 = 3\cdot82 \pm 0\cdot02$ A).

[VS = very strong; VW = very weak; M = medium; S = strong; W = weak]

Estimated intensity	d	hkl	Estimated intensity	d	hkl
W	3.8	100	VW	1.286	300-221
VS	2.70	110	M	1.207	310
W	2.20	111	VW	1.099	222
S	1.905	200	W	0.9562	400
VW	1.710	210	S	.9001	411-330
S	1.558	211	VW	.8755	331
M	1.348	220	M	.8560	420

TABLE 3.

POWDER DIFFRACTION DATA ON $Na_2 CaSiO_4$ (Cubic $a_0 = 7.58$ A).

[VS = very strong; VW = very weak; M = medium; S = strong; W = weak]

Estimated intensity	d	hkl	Estimated intensity	d	hkl
S	4.38	111	M	1.327	440
VW	3.79	200	W	1.269	531
VS	2.68	220	M	1.186	620
M	2.170	222	VW	1.141	533
S	1.879	400	VW	1.083	444
S	1.533	422	VW	1.049	711-551
W	1.444	511-333	M	1.001	642

TABLE 4.

POWDER DIFFRACTION DATA ON $Sr_3Al_2O_6$ (Cubic $a_0 = 15.82$ A).

[VS = very strong; VW = very weak; M = medium; S = strong; W = weak]

Estimated intensity	d	hkl	Estimated intensity	d	hkl
W	5.6	220	VW	1.868	822-660
VW	4.3	123	W	1.773	840
VW	3.96	400	VW	1.684	664
VW	3.48	124	VS	1.616	844
VS	2.81	440	S	1.400	880
M	2.50	620	W	1.317	884-1200
M	2.28	444	W	1.285	10.64
M	2.111	642			12 22
S	1.975	800	S	1.254	12.40

investigations[1, 3] have reported complete structural analyses for $CaTiO_3$ and Na_2CaSiO_4. A comparison of these two known structures would be expected to reveal what they had in common that caused the strong lines of a body-centred lattice with $a_0 = 3.81$ A. In this way the similar strong lines in the pattern of $Ca_3Al_2O_6$ might be explained.

The diffraction data for $CaTiO_3$ are given in *Table 2*. These data indicate a cubic unit cell with $a_0 = 3.81$ A. The lines with $h + k + l = 2n$ (those of a body-centred lattice) are the stronger. Barth[3] showed that this compound has one molecule to the unit cell and arrived at a structure with a Ti atom at the centre and a Ca atom at each corner of the unit cell. Both the Ca and Ti atoms contribute to the strength of the reflections from planes with $h + k + l = 2n$, whereas the reflections from these atoms are out of phase in other planes. This would cause the lines representing a body-centred pattern to be relatively strong. Since the oxygen atoms are placed at $1/2$, $1/2$ 0, $1/2$ 0 $1/2$, and 0 $1/2$ $1/2$, the Ti atom is surrounded by six and the Ca atom by twelve equally distant O atoms.

The diffraction data for Na_2CaSiO_4 given in *Table 3* represent a cubic compound with $a_0 = 7.62$ A. It is found that here, as in $CaTiO_3$, the strong lines are those of a body-centred cube with $a_0 = 3.81$ A. Barth and Posnjak[1] worked out the atomic positions in this structure and found that, with four molecules per cell, Na, Ca, and Si atoms were at or near the corners and centres of cubes representing one-eighth of the full cell. Here again, as in $CaTiO_3$, all heavy atoms contribute to reflections of planes which could result from a body-centred cube of 3.81 A, while the reflections from these atoms are out of phase in other planes. The oxygen arrangement in this compound is completely different from that of $CaTiO_3$. In Na_2CaSiO_4 both Si and Ca atoms are surrounded tetrahedrally, and these groups form chains by the sharing of common O atoms. This is a structure derived from that of high cristobalite by the substitution of Ca atoms for Si and the placing of Na atoms in the large open spaces.

From this discussion it is evident that $CaTiO_3$ and Na_2CaSiO_4 have a cation arrangement in common, consisting of relatively heavy atoms at or near the corners and centres of cubes with an edge of 3.81 A. The strong lines of the powder diffraction pattern of both compounds are therefore those of a body-centred cube with $a_0 = 3.81$ A. However, the important and differentiating aspects of the structure, namely, the oxygen co-ordination of the cations, are not shown by these strong lines. From similarities of the positions of strong lines in the patterns of $CaTiO_3$ and Na_2CaSiO_4 with those in the pattern of $Ca_3Al_2O_6$, it may be assumed that $Ca_3Al_2O_3$ also has a similar structure, with relatively heavy atoms (in this case Ca and Al) at or near the centres and corners of 3.81 A cubes. From the similarity of these lines alone, however, no deductions can be made in regard to the oxygen arrangement.

Harrington found that a density determination indicated three molecules of $Ca_3Al_2O_6$ in a cell with $a_0 = 7.62$ A. In the cell with $a_0 = 15.24$ A there are $8 \times 3 = 24$ molecules. This would give 72 Ca, 48 Al, and 144 O atoms. Since there are 64 of the 3.81 A cubes in a full unit cell, there must be some vacant

spaces, because the total of Ca and Al atoms lacks eight of filling all corner and centre points.

A confirmation of this placing of the metallic atoms is found by a comparison of intensities of certain similar lines in the patterns of $Sr_3Al_2O_6$ and $Ca_3Al_2O_6$, compounds which appear to be isostructural. The diffraction data pertaining to $Sr_3Al_2O_6$ are given in *Table* 4. In this pattern, made under conditions identical with those pertaining to the pattern of $Ca_3Al_2O_6$, it is seen, for example, that the 400 and 840 reflections are strong enough to register, while they do not appear in the pattern of $Ca_3Al_2O_6$. An arrangement of the heavy atoms as outlined would give such a result. To account for this, consider 48 Al atoms and 16 Ca (or Sr) atoms at the centres of the 64 small cubes (such positions in the full cell as 1/8 1/8 1/8, 1/8 3/8 5/8, 5/8 7/8 1/8, etc.). The other 56 Ca (or Sr) atoms are then at corners of the small cubes (such positions as 0 0 0, 1/4 1/2 3/4, 3/4 1/2 0, etc.). Since the contribution of the oxygen atoms to the intensities would be very similar in both $Ca_3Al_2O_6$ and $Sr_3Al_2O_6$, consider only the contribution of the heavy atoms. The intensity factor, then, for the 400 and 840 planes would be

$$56\bar{R} - 16\bar{R} + 48\bar{Al},$$

where $\bar{R}$ is the F (scattering power) value for Ca or Sr atoms and $\bar{Al}$ is the F value for Al atoms for the particular reflection involved. The F values of Al and Ca are very nearly the same, so that the intensity resulting from the metal atoms would be rather small in $Ca_3Al_2O_6$ compared with that in $Sr_3Al_2O_6$, since the scattering power of Sr is about three times that of Al.

No conclusions can be drawn concerning the oxygen arrangement in $CaTiO_3$ and Na_2CaSiO_4 from a consideration of the strong lines in their diffraction patterns. It may be that the oxygen arrangement in $Ca_3Al_2O_6$ is not like that in either of these compounds. This would appear probable when it is noted that in a 3·81 A cube of $CaTiO_3$ there are three O atoms, while in Na_2CaSiO_4 there are only two and in $Ca_3Al_2O_6$ there are two and a-quarter O atoms in the same volume.

Brandenberger[4] has classified cations as : (1) active, having low co-ordination numbers, such as Si and Al ; and (2) inactive, with large co-ordination numbers, such as Na. Structures with both classes are made up of oxygen polyhedrons surrounding cations of the first class, while cations of the second class complete the valence saturation and are placed in the large spaces with high oxygen co-ordination. If the activity of the calcium atoms of $Ca_3Al_2O_6$ is considered, especially with regard to action with water, it is probable that in this compound, as in Na_2CaSiO_4, the Ca atoms, in part at least, are of the first, or active, category and have low oxygen co-ordination.

Structure of Glass in Clinker.

Brownmiller[5] prepared a series of mixtures having compositions near those of the liquids present during the heating of Portland cement clinker. These mixtures all contained the oxides CaO, SiO_2, and Fe_2O_3, and in addition some had Al_2O_3. He then quenched small charges of melts of these various mixtures at two different rates. The faster quench, called instantaneous, gave in all cases isotropic products which produced no X-ray diffraction patterns. The slower quench, in

which the charge stayed on the surface of the mercury and the cooling was considerably slower than in the first method, gave isotropic products, of higher index of refraction than the correspondingly fast quench. Microscopic examination of the slowly-quenched material failed to reveal the presence of any crystal phases. This material produced an X-ray powder pattern consisting of the strong lines of $Ca_3Al_2O_6$. This same pattern was obtained by him even in those mixtures in which no Al_2O_3 was present. The pattern, reproduced in this laboratory by similar methods, had sharp, but in most cases rather weak, lines. Brownmiller considered this material, which gave the pattern, to be a "metastable phase." By this he indicated a structure lacking the complete randomness of glass but still having some degree of irregularity.

It would seem impossible to have sharp lines resulting from a structure with any degree of randomness. Even if the structure consisted of an oxygen network with the other atoms at random, as described by Brownmiller, the different interatomic distances Fe-O, Ca-O, Si-O, and Al-O would result in a low degree of periodicity and a pattern consisting of broad lines. Therefore it seems probable that the patterns in these slowly-quenched samples are not the result of a semi-glass material but of submicroscopic quench growths of a crystal phase. The identity of this phase is not known, but in this present work various compounds have been mentioned which give similar strong lines, and doubtless others exist. Also, it is known that at high temperatures compounds form and can exist which would not be present at equilibrium conditions at lower temperatures. It is quite possible that there exists such a compound as $Ca_3Fe_2O_6$ which would very likely be isostructural with $Ca_3Al_2O_6$. From these considerations it seems very probable that the pattern obtained by Brownmiller from slowly-quenched glasses is not due to a pseudo-crystalline arrangement but to submicroscopic quench growths of a metastable compound.

[1] T. F. W. Barth and E. Posnjak, *Silicate structures of the cristobalite type*, Z. Krist. **81,** 370 (1932).

[2] R. W. G. Wyckoff and G. W. Morey, *X-ray diffraction measurements upon compounds in the system soda-lime-silica*, Am. J. Sci. [5] **212,** 419 (1926).

[3] T. Barth, *The crystal structure of perovskite and related compounds*, Norsk Geol. Tids. **8,** 201 (1925).

[4] E. Brandenberger, Schweizer Archiv. angew. Wiss. Tech. **2,** 24 (1936).

[5] L. T. Brownmiller, *The structure of the glassy phase in Portland cement clinker*, Am. J. Sci. [5] **35,** 241 (1938).

Phase-Equilibria Studies Involving Potash.

(Concluded from March.)

A comparison of the chemical analysis of the preparation with the theoretical composition of $K_2O.23CaO.12SiO_2$ is given in *Table 2*. The amounts of SiO_2 and of combined CaO (61·11 per cent.) are slightly less than their respective theoretical values, but that of K_2O is slightly more. The presence of the extraneous material mentioned may have been the result of the slight deficiency of SiO_2 and CaO, the excess of K_2O, and the presence of the small amounts of R_2O_3.

A microscopical examination of a powdered sample of this preparation showed that $K_2O.23CaO.12SiO_2$ was present as irregularly shaped, somewhat rounded,

TABLE 2.—COMPARISON OF THE CHEMICAL ANALYSIS OF A PREPARATION OF
$K_2O.23CaO.12SiO_2$ WITH THE THEORETICAL COMPOSITION.

Constituent	Preparation I	Theoretical $K_2O.23CaO.12SiO_2$
	%	%
CaO	61. 51	61. 28
SiO₂	33. 55	34. 25
K₂O	4. 60	4. 48
R₂O₃	. 38	
Free CaO	. 4	

TABLE 3.—OPTICAL PROPERTIES OF $K_2O.23CaO.12SiO_2$, α- AND β-$CaO.SiO_2$ AND $3CaO.SiO_2$.

Compound	Optical character	Index of refraction		
		α	γ	Double refraction
$K_2O.23CaO.12SiO_2$	Uniaxial positive	1. 695	1. 703	0. 008
α-$2CaO.SiO_2$	Biaxial positive	1. 715	1. 737	. 022
β-$2CaO.SiO_2$	do	1. 717	1. 735	. 018
$3CaO.SiO_2$	do	Mean=1. 715		. 005

grains exhibiting complex polysynthetic twinning similar to that of α-$2CaO.SiO_2$ but having lower refractive indexes and birefringence than that compound.

A comparison of the optical properties of $K_2O.23CaO.12SiO_2$ with those of α- and β-$2CaO.SiO_2$ and of $3CaO.SiO_2$ is given in *Table 3*. It was not possible to measure accurately the refractive indexes of most of the grains of $K_2O.23CaO.12SiO_2$ because of the complex twinning, accordingly the values given in *Table 3* were obtained from grains less complexly twinned. *Fig. 2* is a photomicrograph of a powder sample of this preparation in transmitted ordinary light. *Fig. 3* shows the same field between crossed nicols.

A comparison, given in *Table 4*, of the interplanar spacings of the X-ray diffraction pattern obtained from a powdered sample of this preparation with that of β-$2CaO.SiO_2$ shows the absence of most of the lines characteristic of
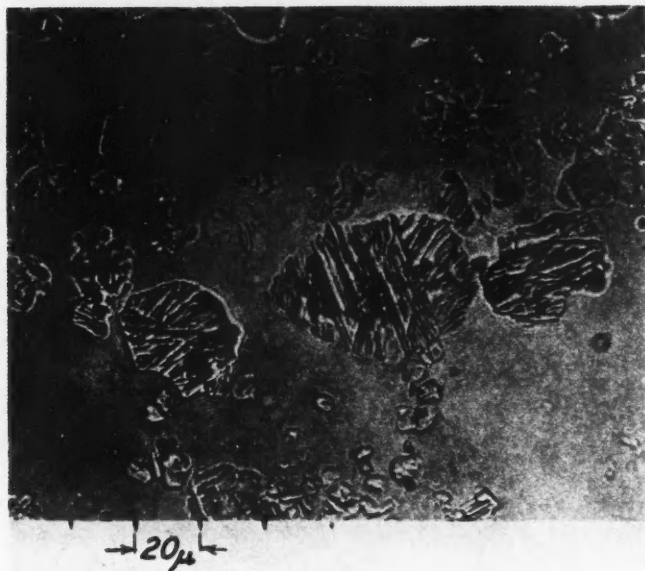
Fig. 2.—Crystals Having Probable Formula $K_2O.23CaO.12SiO_2$
(Ordinary Transmitted Light.)

Fig. 3.—Crystals Having Probable Formula $K_2O.23CaO.12SiO_2$
(Same field as Fig. 2 but between crossed nicols.)

TABLE 4.—INTERPLANAR SPACINGS OF THE DIFFRACTION PATTERNS OF β-2CaO.SiO$_2$ AND K$_2$O.23CaO.12SiO$_2$.

β-2CaO.SiO$_2$		K$_2$O.23CaO.12SiO$_2$		β-2CaO.SiO$_2$		K$_2$O.23CaO.12SiO$_2$	
D$_{hkl}$	Estimated relative intensity	D$_{hkl}$	Estimated relative intensity	D$_{hkl}$	Estimated relative intensity	D$_{hkl}$	Estimated relative intensity
A		A		A		A	
3.97	w [1]			1.902	w		
3.35	w			1.846	vw		
3.06	w			1.802	w-b	1.805	w
2.88	w					1.789	w
2.79	vs			1.726	vw		
2.73	vs	2.75	vs-b			1.717	w
2.66	vw	2.63	w	1.708	w		
2.606	m			1.690	vw		
2.556	vw			1.665	vw		
2.460	w			1.635	m		
2.410	w					1.632	vw
2.291	w	2.29	w	1.613	m		
		2.240	w			1.593	m
2.217	vw			1.590	w		
2.195	s			1.576	w		
		2.185	m	1.553	w		
2.159	vw			1.528	w		
2.130	vw			1.486	w	1.484	vw
2.083	vw			1.451	vw		
2.048	w			1.429	vw		
		2.034	m	1.420	vw		
2.017	w					1.417	vw
1.984	m			1.398	w		
		1.959	s	1.373	m		
1.924	vw					1.370	w-b

[s = strong ; vs = very strong ; m = medium ; w = weak ; vw = very weak ; b = broad.]

β-2CaO.SiO$_2$, and the presence of 10 lines not found in the pattern of β-2CaO.SiO$_2$. The differences between the patterns of 3CaO.SiO$_2$[6] and K$_2$O.23CaO.12SiO$_2$ are even more marked.

State of Combination of K$_2$O in Portland Cement Clinker.

As already stated, K$_2$O.Al$_2$O$_3$ is the only stable compound of K$_2$O in that part of the K$_2$O-CaO-Al$_2$O$_3$ system which is of interest in the study of Portland cement clinker. As a further step in the determination of the state of combination of K$_2$O in clinker, it is important to discover whether K$_2$O.Al$_2$O$_3$ or some other compound containing K$_2$O is stable in that part of the five-component system, K$_2$O-CaO-Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$, related to cement clinker composition.

For the preliminary work on this problem, mixtures within the range of 99 per cent. of 3CaO.SiO$_2$ and per cent. of K$_2$O.Al$_2$O$_3$ to 85 per cent. of 3CaO.SiO$_2$ and 15 per cent. of K$_2$O.Al$_2$O$_3$ were prepared. Because it was observed that liquid was first formed in the charges at some temperature between 1,400 deg. and 1,450 deg. C., the samples were heated at 1,450 deg. C. for 10 minutes, cooled to 1,400 deg. C. at the rate of $\frac{1}{2}$ deg. C. per minute, and then quenched. The compound K$_2$O.Al$_2$O$_3$, which is formed in the K$_2$O-CaO-Al$_2$O$_3$ system, was not positively identified in any of the completely crystallised charges in which the

[6] L. T. Brownmiller and R. H. Bogue, B.S J. Research 3 (1930) RP233 ; Am. J. Sci. 20, 241 (1930).

molar ratio of $3CaO.SiO_2$ to $K_2O.Al_2O_3$ was greater than 6:1 (87·5 per cent. of $3CaO.SiO_2$ and 12·5 per cent. of $K_2O.Al_2O_3$). Large amounts of a birefringent phase with a mean index of about 1·70 were observed. Tricalcium aluminate and much uncombined CaO were present also. Tricalcium silicate was identified only in charges resulting from mixtures originally containing 95 per cent. or more of $3CaO.SiO_2$. The amounts were small and probably represented the excess of $3CaO.SiO_2$ in the reaction with $K_2O.Al_2O_3$. In mixtures having the molar ratio $3CaO.SiO_2 : K_2O.Al_2O_3$ of 6 : 1 or less, the amounts of the new crystalline phase appeared to be about the same as in mixtures of higher ratios, but some residual $K_2O.Al_2O_3$ was apparently present in addition to $3CaO.Al_2O_3$ and CaO. Assuming that the new crystalline phase which is the product of these reactions has the composition $K_2O.23CaO.12SiO_2$, the following equation expresses the reaction occurring when the 12 : 1 ratio mixture (93 per cent. of $3CaO.SiO_2$ and 7 per cent. of $K_2O.Al_2O_3$) was heated :

$$12\ (3CaO.SiO_2) + K_2O.Al_2O_3 \rightarrow K_2O.23CaO.12SiO_2 + 3CaO.Al_2O_3 + 10CaO$$
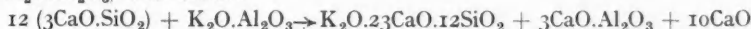
In mixtures having $3CaO.SiO_2 : K_2O.Al_2O_3$ ratios less than 12 : 1, there is an excess of $K_2O.Al_2O_3$ present, but this may not always be identified in the heated charges because of the relatively small percentage of this compound associated with the reaction products. Thus, in the charge resulting from the heating of a mixture having a 6 : 1 ratio, the weight of the $K_2O.Al_2O_3$ calculated to be present is only 6·3 per cent. of the total. The distribution of this amount of $K_2O.Al_2O_3$ as interstitial material throughout the specimen would render identification difficult.

Base mixtures of $2CaO.SiO_2$ and $K_2O.Al_2O_3$ within the range of molar ratios of $2CaO.SiO_2$ to $K_2O.Al_2O_3$ of 1 : 1 to 10 : 1, respectively, were prepared and given the same thermal treatment as the mixtures of $3CaO.SiO_2$ and $K_2O.Al_2O_3$. Microscopical examinations indicated that the new crystalline phase, found as a product of the reactions between $3CaO.SiO_2$ and $K_2O.Al_2O_3$, was formed in the $2CaO.SiO_2$-$K_2O.$-Al_2O_3 reactions also. No $3CaO.Al_2O_3$ or free CaO was observed, but some $K_2O.Al_2O_3$ was identified in charges having a low $2CaO.SiO_2 : K_2O.Al_2O_3$ ratio. As the ratio of $2CaO.SiO_2 : K_2O.Al_2O_3$ increased, the amount of new crystalline phase increased until a ratio of about 6 : 1 or 7 : 1 was reached, charges of these ratios appearing to consist largely of the new crystalline product together with an apparently crystalline but unidentifiable material with low refractive index occurring as veinlets. Again assuming that $K_2O.23CaO.12SiO_2$ is a product of these reactions, it is likely that $CaO.Al_2O_3$ and some residual $K_2O.Al_2O_3$ existed in the charges as the thin veins of unidentified material to which reference has been made.

Since it was found that CaO and $3CaO.Al_2O_3$ were two of the products of reaction of $3CaO.SiO_2$ and $K_2O.Al_2O_3$, and that neither was identified in the reaction products of $2CaO.SiO_2$ and $K_2O.Al_2O_3$, it is reasonable to expect that at some definite proportion of the two calcium silicates and $K_2O.Al_2O_3$ the amount of CaO derived from the silicates will be just equal to the amount required by the Al_2O_3 to form $3CaO.Al_2O_3$. Accordingly, in the preliminary work, various

mixtures of the two silicates with $K_2O.Al_2O_3$ were studied. As a typical case, it was found that a completely crystallised sample, resulting from a mixture corresponding to 2 molecules of $3CaO.SiO_2$, 4 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O.Al_2O_3$, contained the same principal phase observed before, a few grains of $3CaO.Al_2O_3$, a small amount of uncombined CaO, and some residual $K_2O.Al_2O_3$. The exact proportions were not attained, however, until after the discovery of the compound $K_2O.23CaO.12SiO_2$ in the

$$2CaO.SiO_2-K_2O.CaO.SiC_2$$
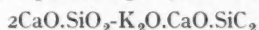
system. A charge consisting of the equivalent of 2 molecules of $3CaO.SiO_2$, 10 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O.Al_2O_3$ was prepared, and after heat treatment, examined by both the powder and polished thin-sections methods. It appeared to consist of two phases only, the more abundant phase being the new crystalline compound and the less abundant phase being $3CaO.Al_2O_3$. The mean index of refraction of the major phase was about 1·70 and the birefringence about 0·01. This reaction may be expressed as

$$2(3CaO.SiO_2)+10(2CaO.SiO_2)+K_2O.Al_2O_3 \rightarrow K_2O.23CaO.12SiO_2+3CaO.Al_2O_3.$$
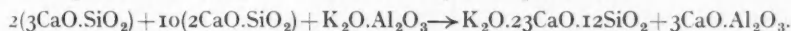
The results of these tests indicate the probable formation of $K_2O.23CaO.12SiO_2$ in completely crystallised preparations having compositions in the

$$K_2O-CaO-Al_2O_3-SiO_2$$

system pertinent to those of Portland cement clinker.

It has been indicated that the compound $K_2O.23CaO.12SiO_2$ can exist in laboratory clinker containing the oxides K_2O, CaO, Al_2O_3, and SiO_2 in amounts likely to be found in Portland cement clinker. In addition to these oxides, Fe_2O_3 is present in the commercial product. Accordingly an additional mixture was prepared including this other principal oxide, Fe_2O_3. This mixture, represented by $3(3CaO.SiO_2) + 9(2CaO.SiO_2) + K_2O.Al_2O_3 + Fe_2O_3$, was heated to 1,400 deg. C. and cooled to 1,295 deg. C. at a rate of 2·5 deg. C. per minute. The completely crystallised product apparently consisted of only two phases— probably $K_2O.23CaO.12SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$.

The maximum and minimum refractive indexes, 1·722 and 1·713, of the potash compound in this charge are considerably higher than those of $K_2O.23CaO.12SiO_2$ in iron-free charges, possibly because of limited solid solution with an iron compound. Although this increase in indexes makes difficult the distinction of the potash compound from $3CaO.SiO_2$ and β-$2CaO.SiO_2$, the maximum index of refraction of the iron-bearing $K_2O.23CaO.12SiO_2$ is lower than that of β-$2CaO.SiO_2$ (1·735) and the double refraction (·009) is somewhat higher than that of pure $3CaO.SiO_2$ (·005).

Another charge was prepared by adding 25 per cent. of $4CaO.Al_2O_3.Fe_2O_3$ to the mixture represented by 2 molecules of $3CaO.SiO_2$, 10 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O_3Al_2O_3$, and the resulting mixture was heated to 1,550 deg. C. and cooled slowly to 1,260 deg. C. The product appeared to consist of $K_2O.23CaO.12SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ only. Thus there has been no indication that any compound of potash other than

$K_2O.23CaO.12SiO_2$ exists under equilibrium conditions in Portland cement clinker in so far as the major oxide constituents are concerned.
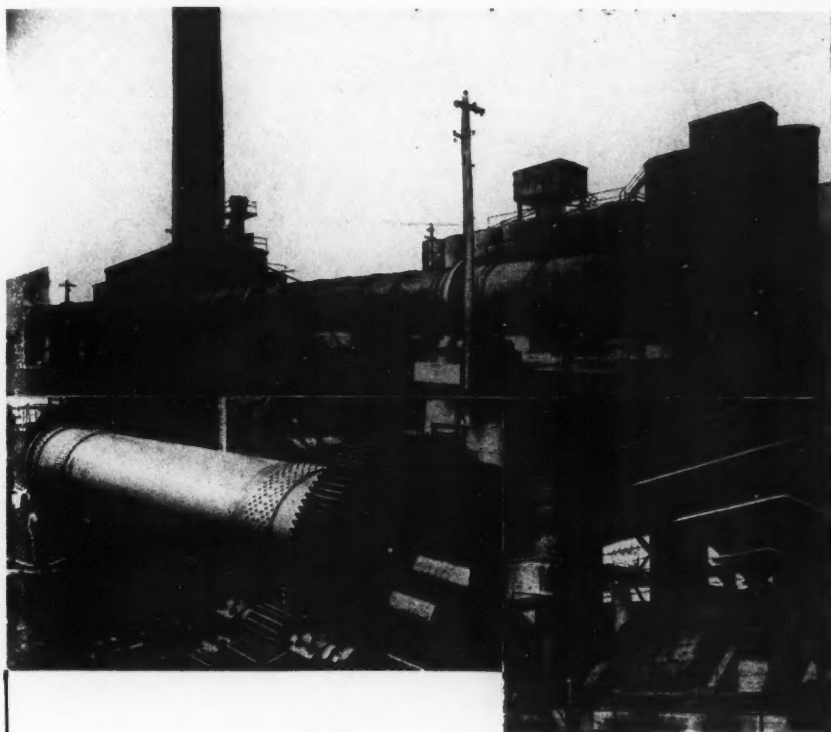
These results explain data obtained in an unpublished investigation conducted by the author in 1929. It was observed that greater difficulty was experienced in obtaining complete combination of the CaO with the other oxide constituents of laboratory clinker mixtures during calcination when K_2O was substituted for like percentages of CaO, that is to say, the amounts of free CaO in the clinkers after calcination at a definite temperature for a definite time increased with increasing amounts of substituted K_2O. These results are shown in *Table* 5. The oxide compositions of the raw mixtures calculated to the clinker basis and the oxide compositions of the clinkers assuming a loss of 30 per cent. of the potash on heating are given. The assumption is based on the amounts of K_2O which were lost from five representative charges analysed after heating in the open platinum boats, as also indicated in *Table* 5. The potential compound compositions, considering the K_2O combined as $K_2O.23CaO.12SiO_2$, have been calculated and are given in *Table* 5. The reasons

TABLE 5.—EFFECT OF THE SUBSTITUTION OF K_2O FOR CaO ON THE COMBINATION OF
CaO IN LABORATORY CEMENT MIXTURES.

Mixture No.	Oxide composition of raw mixture (clinker basis)					Oxide composition based on 30-percent loss of K_2O during heating					Potential compound composition						Uncombined CaO after being heated at—			
	CaO	Al_2O_3	Fe_2O_3	SiO_2	K_2O	CaO	Al_2O_3	Fe_2O_3	SiO_2	K_2O	C_3S	C_2S	$KC_{23}S_{12}$	C_3A	C_4AF	CaO	1,400 °C	1,450 °C	1,500 °C	1,525 °C
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	66.0	11.0	0	23.0	0	66.0	11.0	0	23.0	0	19.5	51.3	0	29.2	0	0	....	0.7	0.0	0.0
2	65.0	11.0	0	23.0	1	65.20	11.03	0	23.07	0.7	17.3	37.8	15.7	29.2	0	0	....	.2	.1	....
3	64.0	11.0	0	23.0	2	64.39	11.07	0	23.14	1.4	15.0	24.4	31.3	29.3	0	0	....	3.5	2.6	....
4	63.0	11.0	0	23.0	3	63.57	11.10	0	23.21	2.1	13.0	10.6	47.0	29.4	0	0	....	5.3	2.8	2.6
5	67.0	10.0	0	23.0	0	67.0	10.0	0	23.0	0	30.5	43.0	0	26.5	0	0	7.7	1.8	0.3	0.0
6	66.0	10.0	0	23.0	1	66.20	10.03	0	23.07	0.7	28.2	29.6	15.7	26.6	0	0	6.7	0.7	.5	....
7	65.0	10.0	0	23.0	2	65.39	10.06	0	23.14	1.4	25.8	16.2	31.3	26.7	0	0	7.4	5.4	4.5	3.1
8	64.0	10.0	0	23.0	3	64.58	10.09	0	23.21	2.1	23.3	3.0	47.0	26.7	0	0	8.0	7.5	7.0	4.3
9	67.0	7.5	2.5	23.0	0	67.0	7.5	2.5	23.0	0	44.0	32.8	0	15.6	7.6	0	2.0	1.1	0.4	0.0
10	66.0	7.5	2.5	23.0	1	66.20	7.52	2.51	23.07	0.7	41.5	19.6	15.7	15.7	7.6	0	2.0	1.6	.9	.7
11	65.0	7.5	2.5	23.0	2	65.39	7.54	2.52	23.14	1.4	39.2	6.1	31.3	15.7	7.7	0	6.2	4.3	3.7	3.6
12	64.0	7.5	2.5	23.0	3	64.58	7.56	2.53	23.21	2.1	27.2	0	47.0	15.7	7.7	2.4	9.7	7.3	6.9	6.8
13	68.8	9.0	0	22.2	0	68.8	9.0	0	22.2	0	50.7	25.5	0	23.9	0	0	....	3.4	2.3	0.1
14	67.8	9.0	0	22.2	1	68.0	9.03	0	22.27	0.7	48.2	12.3	15.7	23.9	0	0	....	1.9	1.0	.5
15	66.8	9.0	0	22.2	2	67.20	9.06	0	22.34	1.4	44.2	0	31.3	24.0	0	0.4	....	6.6	5.4	3.5
16	65.8	9.0	0	22.2	3	66.40	9.08	0	22.40	2.1	24.1	0	47.0	24.1	0	4.8	....	9.8	8.4	7.9

* Amounts of K_2O volatilized in 5 representative clinkers are as follows:

Mix No.	Original K_2O	K_2O in clinker calcined at indicated temperature		Percentage loss of K_2O
	%	%	°C	%
1	1.0	0.75	1,450°	25
4	3.0	1.96	1,500°	35
8	3.0	1.97	1,500°	34
12	3.0	2.15	1,500°	28
15	2.0	1.52	1,450°	24

for the increased difficulty in obtaining complete combination of the CaO with the other oxides, as shown by increased amounts of uncombined CaO remaining in the clinkers, become apparent after a consideration of the changes in the ultimate compositions resulting from the introduction of K_2O. The substitution of K_2O for CaO resulted in greatly increased $3Ca.O.SiO_2$-$2CaO.SiO_2$ ratios because of the formation of $K_2O.23CaO.12SiO_2$. In three cases no $2CaO.SiO_2$ was present and CaO was an equilibrium product (Nos. 12, 15, 16). The formation of $2CaO.SiO_2$ is very rapid at temperatures of 1,400 deg. C. and above. Tricalcium silicate, for the most part, results from the reaction

$$2CaO.SiO_2 + CaO \longrightarrow 3CaO.SiO_2 ;$$
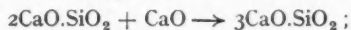
but this reaction becomes more and more sluggish as the amount of $2CaO.SiO_2$ decreases, and equilibrium is attained with greater difficulty. The existence of the compound $K_2O.23CaO.12SiO_2$ explains why, for example, the introduction of $2\cdot1$ per cent. of K_2O into a mixture caused an increase in the amount of uncombined CaO, from $0\cdot1$ to $7\cdot9$ per cent. remaining after calcination at 1,525 deg. C., even though the total CaO had been decreased from $68\cdot8$ to $66\cdot4$ per cent. (Nos. 13 and 16).

As shown in *Table* 5, the addition of small amounts of K_2O to clinker mixtures causes marked changes in the relative amounts of the calcium silicates. Thus, for example, 1 per cent. of K_2O may react with $21\cdot9$ per cent. of $2CaO.SiO_2$ to form $22\cdot3$ per cent. of $K_2O.23CaO.12SiO_2$ with the liberation of $0\cdot6$ per cent. of CaO. This $0\cdot6$ per cent. of CaO in turn combines with $1\cdot9$ per cent. of additional $2CaO.SiO_2$ to form $2\cdot5$ per cent. of $3CaO.SiO_2$, $23\cdot8$ per cent. of $2CaO.SiO_2$ having been removed from the mixture by the introduction of 1 per cent. of K_2O. In a mixture in which the potential $2CaO.SiO_2$ is less than $23\cdot8$ per cent., the remaining K_2O reacts with the $3CaO.SiO_2$ to form $K_2O.23CaO.12SiO_2$ and CaO. Under these conditions free CaO is present as an equilibrium product ; 1 per cent. of K_2O reacting with $29\cdot1$ per cent. of $3CaO.SiO_2$ to liberate $7\cdot7$ per cent. of CaO.

Inspection of the amounts of K_2O and of free CaO in certain analysed commercial clinkers employed in other investigations by this laboratory, however, revealed a few cases in which the determined free CaO was less than that calculated, assuming all of the K_2O combined as $K_2O.23CaO.12SiO_2$. This has suggested that some of the K_2O may have reacted with the minor acidic constituents of these clinkers and reduced the amount of potash available for the formation of $K_2O.23CaO.12SiO_2$, the final result being a reduction in the amount of free CaO in the clinker. For example, if all of the SO_3 in a clinker containing $0\cdot2$ per cent. of SO_3 reacted with K_2O, the amount of the latter combined as K_2SO_4 would be about $0\cdot24$ per cent. The reaction of this quantity of K_2O with SO_3 rather than with CaO and SiO_2 would decrease the amount of free lime in the clinker by about $1\cdot8$ per cent.

Additional studies of systems involving potash and minor constituents of clinker are now in progress, and there are indications that such materials may produce marked effects on the constitution of clinker. Evidence that $K_2O.23CaO.12SiO_2$ reacts with $CaSO_4$ to form $2CaO.SiO_2$ and K_2SO_4 has been

obtained. Recent microscopical examinations of commercial clinkers have revealed the presence of K_2SO_4 in many cases.

The compound $K_2O.23CaO.12SiO_2$ has not yet been identified definitely in commercial clinkers by means of microscopical examinations. This may have been due to (1) lack of equilibrium during cooling of the clinker resulting in the formation of an unstable compound or of glass containing potash, (2) the reaction of most of the potash present with minor acidic oxides, such as SO_3, (3) mistaken identification in powdered specimens due to the similarity in the indexes of refraction to those of the calcium silicates, (4) mistaken identification due to the similarity of the etching characteristics of the potash compound with those of one or the other, or both, of the calcium silicates.

Summary.

A portion of the system $2CaO.SiO_2$-$K_2O.CaO.SiO_2$ has been investigated by the phase-equilibrium method and the results are presented. A temperature-concentration diagram for the binary system, incomplete because of the temperature limitations of the furnace employed, has been constructed.

One intermediate compound was found in the system, having the composition $K_2O.23CaO.12SiO_2$. The reported optical properties and the interplanar spacings of the X-ray diffraction pattern were determined on a preparation having the composition closely approaching that of the theoretical for $K_2O.23CaO.12SiO_2$.

The results of studies on mixtures of $3CaO.SiO_2$ and $K_2O.Al_2O_3$, and of $2CaO.SiO_2$ and $K_2O.Al_2O_3$, indicate that the compound $K_2O.Al_2O_3$, which previously had been shown to be stable in the K_2O-$CaO.Al_2O_3$ and in the K_2O-CaO-Al_2O_3-Fe_2O_3 systems, does not exist in the region of the K_2O-CaO-Al_2O_3-SiO_2 system, which is directly concerned with Portland cement. Possibly these results may be explained by the potash combining with CaO and SiO_2 to form the compound $K_2O.23CaO.12SiO_2$.

The compound $K_2O.23CaO.12SiO_2$ was found to exist in a region of the K_2O-CaO-Al_2O_3-SiO_2-Fe_2O_3 system in which Portland cement compositions fall.

While it is recognised that various minor acidic constituents generally existing in commercial Portland cement clinker may combine with all or part of the potash present, evidence was obtained that K_2O combines as $K_2O.23CaO.12SiO_2$ in the presence of the major constituents CaO, Al_2O_3, SiO_2 and Fe_2O_3, in the proportions occurring in Portland cement, and that this ternary compound will occur in clinker limited to those components prepared under equilibrium conditions of heating and cooling.